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- (54) **Process for the preparation of a basic salt, salt thus prepared and oil compositions containing such a salt.**

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**EP 0 279 493 B1**

## Description

The present invention relates to a process for the preparation of a basic alkaline earth metal salt of a blend of organic carboxylic acids, a salt thus prepared and to oil compositions containing such a salt.

5 The use of alkaline earth metal salts of organic carboxylic acids as additives for lubricating oil compositions is known. The said salts have a dispersant property so that, when applied in such composition, they ensure that the inside of engine cylinders remains clean and that deposition of carbonaceous products on pistons and in piston grooves is counteracted, so that piston-ring sticking is prevented.

10 It is also known to prepare basic (or overbased) alkaline earth metal salts of such acids. The overbasing provides an alkaline reserve which, when applied in lubricating oil compositions, reacts with and neutralises acidic compounds formed during the operation of the engine in which the composition is applied. Hence, sludge which may arise, is maintained dispersed due to the dispersant property of the salt while acids which would enhance sludge formation are neutralised.

15 In British patent specification No. 786,167, a process for the preparation of basic salts is described in which an organic acid is reacted with an excess of an alkaline earth metal oxide or hydroxide in an oil and subsequently carbon dioxide is passed through the reaction mixture to yield basic salts. As suitable acids are mentioned substituted or unsubstituted aliphatic, cycloaliphatic and aromatic acids, comprising carboxylic acids, sulphur-containing acids, phosphoric acids, thio-acids, phenols and partial esters of sulphur-and  
20 phosphorus-containing acids.

In the technical field there is a desire to use products with a basicity as high as possible, i.e. the relative proportion of the organic acid residue in the basic salt is as low as possible. The reason for this is that the costs of the product are mainly incurred by the costs of the organic acid.

The basicity of these products is generally expressed as a basicity index (BI), being defined as the  
25 equivalents ratio of the total of alkaline earth metal to the total of organic acids. The prior art processes normally yield products having a BI of at most 10, and it was found that in the preparation of products having a BI that high or even higher using carboxylic acids a pronounced tendency to gelation occurs, thereby severely hindering the handleability of the products. Another problem was that when using certain acids only relatively low BI values were obtainable. It has now been found that when a blend of two specific  
30 types of carboxylic acids is used, a high BI value can be obtained without incurring gelation problems.

Accordingly, the present invention relates to a process for the preparation of a basic alkaline earth metal salt of a blend of organic carboxylic acids, which comprises

- (a) mixing the organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent;
  - 35 (b) introducing carbon dioxide into the mixture obtained in an amount of at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal; and
  - (c) removing residual solids, if any, and an aqueous layer, if any, wherein
- the organic carboxylic acids comprise a blend of a C<sub>8-30</sub> alkyl salicylic acid and one or more alkanecarboxylic acids in which the alkyl moiety is branched and has from 4 to 40 carbon atoms.

40 Particularly preferred alkyl salicylic acids are those having at least 10 carbon atoms in the alkyl group, in particular from 12 to 26 carbon atoms.

The alkanecarboxylic acid used in the present invention is branched, and has a chain length long enough to avoid any solubility problems in oil compositions such as lubricants, whilst not being too long to incur problems in naphthenic or aromatic oil compositions. Preferably, the alkyl moiety has 8 to 28 carbon  
45 atoms, and in particular is a tertiary alkyl moiety. The tertiary carboxylic acids are especially suitable since when they are used very high BI values can be obtained. Very suitable acids include mixtures of tertiary acids, such as those sold under the trade name "VERSATIC" acids. These acids are prepared by subjecting an olefin, e.g. a propylene oligomer, or a linear mixed olefin such as those sold under the trade name "SHOP" to a Koch reaction, yielding branched carboxylic acids. When mixtures of acids are used the  
50 preferred length of the alkyl moiety relates to the average length of the alkyl groups.

The ratios between the alkyl salicylic acid and the alkane carboxylic acid may vary within wide ranges. Advantageously the equivalent ratio of the alkyl salicylic acid to alkanecarboxylic acid ranges from 10:1 to 1:10, preferably from 4:1 to 1:4.

The alkaline earth metal salts prepared include magnesium, calcium, strontium and barium salts.  
55 Preferably, the alkaline earth metal applied is magnesium or calcium.

The reaction mixture prepared in step (a) of the present process suitably contains a promotor, preferably an oxygen-containing organic solvent and optionally water. Suitable solvents include C<sub>1-8</sub> alcohols, polyhydric alcohols such as glycol, propylene glycol, glycerol or 1,3-dihydroxypropane, ethers

such as C<sub>1-4</sub> monoethers of glycol or propylene glycol, di isopropyl ether, 1,3- or 1,4-dioxane, or 1,3-dioxolane. Preferably the promotor is a C<sub>1-6</sub> alcohol, in particular methanol. It will be appreciated that in industrial processes use may be made of technical solvents, and that the use of technically pure promotors, such as methanol, might incur the presence of water. Hence, in such cases addition of water per se is not required since its addition is made implicitly by the addition of the promotor.

The preparation of the mixture according to step a) of the present process can be carried out in any convenient way, e.g. by mixing the alkaline earth metal hydroxide and/or oxide with the promotor, if used, and adding the acids, whether or not in the presence of the promotor or a hydrocarbon solvent, to the resulting mixture. It is preferred to mix the blend of the acids and the alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent and subsequently add the promotor. The promotor may contain a substantial amount of water. Preferably the water content is adjusted such that the percentage of water in the mixture amounts to 0 to 10%w, based on the total liquids.

The hydrocarbon solvent can be selected from a wide variety of solvents. Suitable solvents include hydrocarbon oils, such as solvent-refined and/or hydrogenated lubricating oils having a kinematic viscosity of 3.5-35 mm<sup>2</sup>/s at 100°C. Preferably it is an aromatic hydrocarbon or a hydrocarbon fraction rich in aromatics, such as gasoline. Suitable hydrocarbon solvents are benzene, toluene, xylene or mixtures thereof, xylene being particularly preferred. The amount of the solvent is not critical. Promotor:solvent volume ratios up to 1 can suitably be applied, preference being given to ratios in the range from 0.1 to 0.6.

The concentration of the organic carboxylic acid in the solvent or solvent mixture can vary within wide limits. Suitably the acids equivalent concentration of acids is from 0.01 to 1 molar equivalent/kilogram, preferably from 0.1 to 0.8, based on the combined weight of organic carboxylic acids and hydrocarbon solvent.

The amount of alkaline earth metal to be added in step a) should be at least 1 equivalent, and is preferably more, so that the subsequent carbon dioxide supply results in very high BI compounds. In that case, the amount of alkaline earth metal hydroxide and/or oxide added in step a) is preferably from 10 to 25 equivalents per equivalent acid.

The temperature at which step a) is carried out is not critical, and may be ambient temperature or elevated temperature. Suitable temperatures include 15-150°C.

In step b) the temperature is advantageously from 15 to 150°C, preferably from 30 to 75°C. In order to obtain the elevated temperature it may be necessary to employ elevated pressures, since the desired reaction temperature may be above the atmospheric reflux temperature of the reaction mixture. Suitable pressures include 1 to 15 bar abs. Higher pressures are possible, but merely add to the costs of the process. The rate at which the carbon dioxide is introduced is advantageously from 0.05 to 1.0 equivalent carbon dioxide per equivalent acid per minute. The carbon dioxide introduction is conveniently carried out by passing carbon dioxide, or a mixture of carbon dioxide with an inert gas, such as air or nitrogen, through the reaction mixture under slightly higher pressure than the pressure prevailing in the reaction mixture. Higher pressures may be employed. Carbon dioxide will be absorbed in the reaction mixture and will react with the alkaline earth metal compounds present therein forming a basic complex salt of the organic acid salt and carbonate, hydroxide and/or oxide. The amount of carbon dioxide to be taken up in step b) is to a certain extent dependent on the amount of alkaline earth metal added in step a) of the present process. Suitably the relative amount of carbon dioxide is somewhat less than the relative amount of alkaline earth metal hydroxide or oxide.

Preferably the introduction of carbon dioxide in step b) is stopped after 0.5 to 0.9 equivalent carbon dioxide per equivalent alkaline earth metal has been taken up. Conveniently, this corresponds with 5 to 23 equivalent carbon dioxide per equivalent acid.

It has been found that an ageing period between step b) and step c) can be advantageous, since it increases the BI of the resulting basic salt. Such an ageing period amounts suitably to at least 15 min. A maximum period is generally imposed by practical and/or economical reasons, and is generally below 20 hours. Preferably the period between steps b) and c) is from 1 to 4 hrs.

The reaction mixture at the end of step b) may be worked up by any method known in the art. It may be subjected to a centrifuging treatment to remove solids comprising unreacted alkaline earth metal hydroxide and/or oxide and/or non-colloidal alkaline earth metal carbonate, if any. The resulting solution may then be subjected to a liquid-phase separation. One liquid phase can be an aqueous layer which may contain the promotor when it is used, the other one is the hydrocarbon solvent plus the basic salts dispersed therein. It is also possible to reverse the above operations.

The present process can be used for the preparation of basic salts having a wide variety of basicity indices. So, it would be possible to prepare basic salts having a relatively low BI e.g. from 1 to 10. The present process, however, is excellently suitable for preparing basic salts having a basicity index from 10 to

20.

The process described is a one-step process. However it is possible to integrate the process according to the present invention in a two-step process, in particular in a two-step process according to Applicants' UK patent application No. 8613815. Thereto, step (a) and (b) are carried out in two stages, a1, a2, b1 and b2 respectively, whereby the stages comprise:

- (a1) preparing a mixture of one equivalent of the blend of the organic carboxylic acids and more than one equivalent of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent;
- (b1) introducing carbon dioxide into the mixture obtained until at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal has been taken up;
- (a2) adding at least one further equivalent of alkaline earth metal hydroxide and/or oxide to the reaction mixture, so that the total amount of alkaline earth metal hydroxide and/or oxide is at least 10 equivalent;
- (b2) resuming the introduction of carbon dioxide to the resulting mixture.

Between stages (b1) and (a2) and after (b2) ageing periods can be employed as is indicated in the above patent application. The ageing period after stage (b2) corresponds with the above-mentioned ageing period between steps (b) and (c).

The process according to the present invention can be carried out batchwise and also in a continuous manner.

The basic salts are excellent dispersant additives in oils. Therefore the present invention also provides oil compositions comprising a major amount of a base oil and a minor amount of a basic alkaline earth metal salt as described hereinbefore. Preferably the base oil is a lubricating base oil, and conveniently constitute more than 50%w of the composition. It can be selected from mineral lubricating oils of varying viscosities, but it also includes a synthetic lubricant, such as ester-type lubricant or a polyolefin-type fluid, or a vegetable oil, or a grease.

Fuel compositions which are used in marine diesel engines usually contain some sulphur compounds. To neutralize the acidic compounds formed from these sulphur compounds a relatively high concentration of the basic salt is employed. Preferably, these marine lubricating oil compositions contain from 5 to 30%w of basic alkaline earth metal salt. Lubricating oil compositions for road engines may contain lower concentrations. The amount of basic alkaline earth metal salt in these lubricating oil compositions is preferably from 0.01 to 5%w, in particular from 0.1 to 4.0%w.

Fuels, such as gasoline, kerosine, diesel fuel and gas oils, can also contain the above basic salts. The amount of these salts is similar to that in road engine lubricating oil compositions or lower; conveniently the amount is from 0.001 to 5%w, in particular from 0.01 to 1.0%w.

The lubricating oil composition can be prepared by mixing a concentrate containing up to 60%w of a basic salt as described above in a lubricating oil, with a lubricating base oil to give the desired concentration. Such a concentrate is conveniently prepared by addition of a lubricating oil to the product obtained after completion of step c), and removal of any volatile hydrocarbon solvent, water and alcohol, if present. The lubricating oil may be the same as the one indicated above as a suitable hydrocarbon solvent. The concentrate may conveniently contain a stabiliser, which is selected from a variety of organic compounds, such as those described in British patent specification No. 818,325. These compounds include mono- or polyhydric alcohols, alkyl amines and alkyl phenols.

The lubricating oil compositions may further contain a number of other additives, such as antioxidants, foam inhibitors, corrosion inhibitors, viscosity index improvers, and pour point depressants, as can be established by a person skilled in the art. In particular, improved properties can be realised by addition of polyisobutene/succinic anhydride adducts, such as LUBAD 349 (sold by Lubrizol).

The invention will be illustrated by means of the following Examples.

#### EXAMPLE 1

The following experiments were carried to show the synergistic effect of using a blend of organic carboxylic acids in the process of the present invention.

#### Comparative Experiment A

1340ml of xylene was mixed with 640g of C<sub>14</sub>-C<sub>18</sub> alkylsalicylic acid (ASA) (0.72 eq) and 400g (10.8 eq) calcium hydroxide. The Ca(OH)<sub>2</sub>/ASA ratio was 15:1. After stirring for 1 hour at 40 °C, 390 ml methanol was added to the reaction mixture, and carbon dioxide was introduced at 50 °C and a rate of 0.12 eq CO<sub>2</sub>/eq acid.min. After an uptake of 9.3 eq CO<sub>2</sub>/eq acid the reaction mixture gelled to become a solid mass. The BI of this solid mass could not be determined, but in theory could only have reached a value of around 10-

11.

Comparative Experiment B

5 This experiment used a mixture of tertiary carboxylic acids, sold under the trade name "VERSATIC 10", which consisted mainly of 3-methyl-octane-3-carboxylic acid together with minor amounts of 4-methyl-octane-4-carboxylic acid, 3-ethyl-heptane-carboxylic acid and 4-ethyl-heptane-4-carboxylic acid. The acid number of this acids mixture was 5.8 meq/g. One equivalent of this mixture was added to xylene, yielding an acid concentration of 0.2 meq/g. Calcium hydroxide was added in an amount of 20 eq. After stirring for 1  
 10 hour, methanol was added to the reaction mixture at 44-55 °C to give 20%vol based on total liquid. CO<sub>2</sub> was introduced at a rate of 0.40 eq CO<sub>2</sub>/eq acid.min, until an uptake of 12 eq CO<sub>2</sub>/eq acid. After settling of the two liquid phases now present, the methanol-water layer was removed. From the xylene layer the residual solids were removed by centrifugation. The BI of the calcium salt present in the xylene layer was 5.3.

15 Experiment 1

The procedure of comparative experiment B was repeated with a mixture of the ASA of experiment A and the V10 acids of experiment B. The relative amounts of the various reactants were 1 equivalent ASA  
 20 per 1 equivalent V10 acid. The concentration of the acids in xylene was 0.4 meq H<sup>+</sup>/g, and the relative amount of calcium hydroxide was 10 equivalent. Methanol, containing 3% vol water, was added in a quantity of 14.4% vol, based on the xylene. Carbon dioxide was introduced into the reaction mixture at a rate of 0.12 eq/eq acid.min at a temperature of 50-55 °C. After an CO<sub>2</sub> uptake of 7.1 eq/eq acid, the reaction mixture was worked up as described in experiment B, yielding a product having a BI of 8.8, without  
 25 gelling.

Experiment 2

A two-step process was carried out by following the procedure of Experiment 1 with the following  
 30 amounts of reactants: ASA to V10 acids equivalents ratio is 7.3; the equivalent ratio of calcium hydroxide to acid is 10:1; the acid concentration, the composition of the solvents mixture, temperature and the CO<sub>2</sub> introduction rate were as described in Experiment 1. After a CO<sub>2</sub> uptake of 7.88 eq/eq acid, the reaction was interrupted for 15 minutes, calcium hydroxide was subsequently added in an amount of 7 eq/eq acid, the reaction mixture was stirred for one hour and the CO<sub>2</sub> introduction was resumed at 50 °C. After a total  
 35 uptake of 12.1 eq CO<sub>2</sub> (in both steps) the reaction mixture was treated as described in Experiment B, yielding a product with a BI of 14.8.

Experiment 3

40 The procedure of Experiment 2 was repeated. After stopping of the CO<sub>2</sub> introduction at the second stage, i.e. after an uptake of 12.1 eq CO<sub>2</sub>, the reaction mixture was subjected to an ageing period of 16 hours while stirring at 50 °C continued. After the work-up procedure as described in Experiment B a product with a BI of 15.1 was obtained.

From these experiments it is apparent that whereas the use of ASA or V10 acids alone yields  
 45 unsatisfactory results, the use of a combination of these acids yield good products with a high BI and without incurring gelation problems. The use of an ageing period increases the BI of the product obtained.

EXAMPLE 2

50 In this Example a combination of ASA and tertiary carboxylic acids mainly having 19 carbon atoms (V19 acids) was used. The carboxylic acids were prepared by subjecting C<sub>18</sub> alpha-olefins to a Koch reaction. The product of this reaction is a mixture of highly branched acids based on the C<sub>18</sub> olefin and its dimer which is formed during the reaction. The acid number of the mixture was 2.28 meq/g. Experiment 4 was carried out as a one step process as Experiment 1. Experiment 5 was carried out as Experiment 4 but with  
 55 the use of a 16hr ageing period as described in Experiment 3. Experiments 6 and 7 were carried out as Experiment 3, i.e. with the use of a 16 hours ageing period.

The acids ratio, the CO<sub>2</sub>-uptake in the various steps and the BI of the products obtained are indicated in Table 1 below.

TABLE 1

Exp. No.	ASA/V19 (eq/eq)	CO <sub>2</sub> uptake (eqCO <sub>2</sub> /eq acid)			BI product (eq/eq)
		1 step	2 step	total	
4	1:1	-	-	12.5	13.7
5	1:1	-	-	12.5	14.2
6	1:1	7.9	4.1	12.0	13.0
7	7:3	7.9	4.6	12.5	14.6

The product of Experiments 4-7 were introduced into a mineral lubricating oil, the mixtures obtained were subjected to vacuum distillation to remove xylene to yield concentrates. The calcium contents and the kinematic viscosities of the concentrates at 100° C are indicated below.

TABLE 2

Prod. of Exp. No.	Ca content %w	V <sub>k</sub> 100 (mm <sup>2</sup> /s)
4	10.1	15.1
5	10.1	12.7
6	9.7	10.2
7	9.8	14.3

EXAMPLE 3

The procedure of Experiment 2 was followed in the following experiments 8 and 9. The differences between the latter experiments and Experiment 2 are as follows. The acids used in an equivalent ratio 1:1 were ASA and a mixture of tertiary carboxylic acids obtained as those described in Example 2 and having an acid number of 1.83 meq/g. In both steps an amount of calcium hydroxide of 12 eq/eq acid was added, i.e. the total calcium hydroxide amounted to 24 eq. In the work-up procedure residual solids were removed by filtration over a filter aid and not by centrifugation. Reaction conditions were as in Experiment 2. The CO<sub>2</sub> uptake and the BI's of the resulting products are given in Table 3.

**TABLE 3**

Exp. No.	CO <sub>2</sub> uptake (eqCO <sub>2</sub> /eq acid)			BI product (eq/eq)
	1 step	2 step	total	
8	9.4	7.7	17.1	18.31
9	9.4	9.6	19.0	18.95

The products of these experiments were taken up in a lubricating oil as described in Example 2. The calcium contents and the kinematic viscosity are indicated below.

**TABLE 4**

Prod. of Exp. No.	Ca content (%w)	V <sub>k</sub> 100 (mm <sup>2</sup> /s)
8	9.9	11.6
9	9.9	12.9

**Comparative Experiment C**

To show that linear carboxylic acids are not suitable for the present process, a combination of stearic acid and ASA was used in a 1:1 equivalent ratio in the following experiment.

To 96.1 g of ASA and 32.0 g of stearic acid in 435.3 g of xylene 141.9 g of calcium hydroxide (17 eq/eq acid) was added together with 91.7 g of methanol and 2.8 g of water. This reaction mixture was subjected to a reaction as described under comparative Experiment B, and at a CO<sub>2</sub> uptake of 8.2 eq/eq acid the CO<sub>2</sub> introduction was interrupted due to severe gelation of the reaction mixture.

**Claims**

**Claims for the following Contracting States : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE**

- Process for the preparation of basic alkaline earth metal salts of organic carboxylic acids, which comprises
  - (a) mixing the organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent;
  - (b) introducing carbon dioxide into the mixture obtained in an amount of at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal; and
  - (c) removing residual solids, if any, and an aqueous layer, if any;
 characterised in that the organic carboxylic acids comprise a blend of a C<sub>8-30</sub> alkyl salicylic acid with one or more alkanecarboxylic acid in which the alkyl moiety is branched and has from 4 to 40 carbon atoms.

2. Process according to claim 1, in which the alkyl salicylic acid has 12 to 26 carbon atoms in the alkyl group.
3. Process according to claim 1 or 2, in which the alkyl moiety of the alkanecarboxylic acid is a tertiary alkyl moiety containing 8 to 28 carbon atoms.
4. Process according to any one of claims 1-3, in which the equivalent ratio of the C<sub>8-30</sub> alkylsalicylic acid:alkane carboxylic acid ranges from 10:1 to 1:10.
5. Process according to any one of claims 1-4, in which the alkaline earth metal is calcium or magnesium.
6. Process according to any one of claims 1-5, in which the amount of alkaline earth metal hydroxide and/or oxide added in step (a) is from 10 to 25 equivalents per equivalent acid.
7. Process according to any one of claims 1-6, in which the mixture in step (a) further comprises an oxygen-containing organic solvent, and optionally water.
8. Process according to claim 7, in which the oxygen-containing organic solvent is a C<sub>1-6</sub> alcohol.
9. Process according to any one of claims 1-8, in which the mixture of the blend of the organic carboxylic acids and alkaline earth metal hydroxide and/or oxide is prepared by mixing the acids and the alkaline earth metal hydroxide and/or oxide in the hydrocarbon solvent
10. Process according claim 9, in which the hydrocarbon solvent is selected from benzene, toluene, xylene, or a mixture thereof.
11. Process according to any one of claims 1-10, in which the introduction of carbon dioxide in step (b) is carried out at a rate of 0.05 to 1.0 equivalent carbon dioxide per equivalent acid per minute.
12. Process according to any one of claims 1-11, in which an ageing period of from 0.25 to 20 hours is present between steps (b) and (c).
13. Process according to any one of claims 1-12, in which steps (a) and (b) are carried out in two stages, the stages comprising:-
  - (a1) preparing a mixture of the blend of organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent;
  - (b1) introducing carbon dioxide into the mixture obtained until at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal has been taken up;
  - (a2) adding at least one further equivalent of alkaline earth metal hydroxide and/or oxide to the reaction mixture, so that the total amount of alkaline earth metal hydroxide and/or oxide is at least 10 equivalent;
  - (b2) resuming the introduction of carbon dioxide to the resulting mixture.
14. Basic alkaline earth metal salt of a blend of organic carboxylic acids whenever prepared according to any one of claims 1-13.
15. Oil composition comprising a major amount of a base oil and a minor amount of a basic alkaline earth metal salt as claimed in claim 14.

**Claims for the following Contracting State : ES**

1. Process for the preparation of basic alkaline earth metal salts of organic carboxylic acids, which comprises
  - (a) mixing the organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent;
  - (b) introducing carbon dioxide into the mixture obtained in an amount of at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal; and



(c) removing residual solids, if any, and an aqueous layer, if any;  
characterised in that the organic carboxylic acids comprise a blend of a C<sub>8-30</sub> alkyl salicylic acid with one or more alkanecarboxylic acid in which the alkyl moiety is branched and has from 4 to 40 carbon atoms.

- 5 2. Process according to claim 1, in which the alkyl salicylic acid has 12 to 26 carbon atoms in the alkyl group.
3. Process according to claim 1 or 2, in which the alkyl moiety of the alkanecarboxylic acid is a tertiary  
10 alkyl moiety containing 8 to 28 carbon atoms.
4. Process according to any one of claims 1 to 3, in which the equivalent ratio of the C<sub>8-30</sub> alkylsalicylic acid:alkane carboxylic acid ranges from 10:1 to 1:10.
- 15 5. Process according to any one of claims 1-4, in which the alkaline earth metal is calcium or magnesium.
6. Process according to any one of claims 1-5, in which the amount of alkaline earth metal hydroxide and/or oxide added in step (a) is from 10 to 25 equivalents per equivalent acid.
- 20 7. Process according to any one of claims 1-6, in which the mixture in step (a) further comprises an oxygen-containing organic solvent, and optionally water.
8. Process according to claim 7, in which the oxygen-containing organic solvent is a C<sub>1-6</sub> alcohol.
- 25 9. Process according to any one of claims 1-8, in which the mixture of the blend of the organic carboxylic acids and alkaline earth metal hydroxide and/or oxide is prepared by mixing the acids and the alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent.
10. Process according to claim 9, in which the hydrocarbon solvent is selected from benzene, toluene,  
30 xylene, or a mixture thereof.
11. Process according to any one of claims 1-10, in which the introduction of carbon dioxide in step (b) is carried out at a rate of 0.05 to 1.0 equivalent carbon dioxide per equivalent acid per minute.
- 35 12. Process according to any one of claims 1-11, in which an ageing period of from 0.25 to 20 hours is present between steps (b) and (c).
13. Process according to any one of claims 1-12, in which steps (a) and (b) are carried out in two stages, the stages comprising:-  
40 (a1) preparing a mixture of the blend of organic carboxylic acids with more than an equivalent amount of an alkaline earth metal hydroxide and/or oxide in a hydrocarbon solvent;  
(b1) introducing carbon dioxide into the mixture obtained until at least 0.5 equivalent carbon dioxide per equivalent of excess alkaline earth metal has been taken up;  
(a2) adding at least one further equivalent of alkaline earth metal hydroxide and/or oxide to the  
45 reaction mixture, so that the total amount of alkaline earth metal hydroxide and/or oxide is at least 10 equivalent;  
(b2) resuming the introduction of carbon dioxide to the resulting mixture.
14. Process for the preparation of an oil composition which comprises mixing a major amount of a base oil  
50 and a minor amount of a basic alkaline earth metal salt of a blend of organic carboxylic acids prepared according to a process as claimed in any one of the preceding claims.

#### Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

- 55 1. Verfahren zur Herstellung von basischen Erdalkalimetallsalzen von organischen Carbonsäuren, welches Verfahren

- (a) ein Mischen der organischen Carbonsäuren, mit mehr als einer äquivalenten Menge eines Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel;  
 (b) ein Einführen von Kohlendioxid in das erhaltene Gemisch in einer Menge von wenigstens 0,5 Äquivalenten Kohlendioxid je Äquivalent Erdalkalimetallüberschuß; und  
 5 (c) Abtrennen etwaiger restlicher Feststoffe und einer wäßrigen Phase, sofern vorhanden, umfaßt; dadurch gekennzeichnet, daß die organischen Carbonsäuren ein Gemisch einer C<sub>8</sub>-<sub>30</sub> Alkylsalicylsäure mit einer oder mit mehreren Alkancarbonsäuren umfaßt, worin der Alkylteil verzweigt ist und 4 bis 40 Kohlenstoffatome aufweist.
- 10 2. Verfahren nach Anspruch 1, worin die Alkylsalicylsäure 12 bis 26 Kohlenstoffatome in der Alkylgruppe aufweist.
3. Verfahren nach Anspruch 1 oder 2, worin der Alkylrest der Alkancarbonsäure ein tertiärer Alkylrest mit 8 bis 28 Kohlenstoffatomen ist.
- 15 4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Äquivalentverhältnis der C<sub>8</sub>-<sub>30</sub> Alkylsalicylsäure:Alkancarbonsäure von 10:1 bis 1:10 beträgt.
5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Erdalkalimetall Calcium oder Magnesium ist.
- 20 6. Verfahren nach einem der Ansprüche 1 bis 5, worin die in Stufe (a) zugesetzte Menge an Erdalkalimetallhydroxid und/oder -oxid von 10 bis 25 Äquivalente je Äquivalent Säure beträgt.
7. Verfahren nach einem der Ansprüche 1 bis 6, worin das Gemisch in Stufe (a) zusätzlich ein sauerstoffhaltiges organisches Lösungsmittel und gegebenenfalls Wasser umfaßt.
- 25 8. Verfahren nach Anspruch 7, worin das sauerstoffhaltige organische Lösungsmittel ein C<sub>1</sub>-<sub>6</sub> Alkohol ist.
9. Verfahren nach einem der Ansprüche 1 bis 8, worin das Gemisch aus der Mischung der organischen Carbonsäuren mit Erdalkalimetallhydroxid und/oder -oxid durch Vermischen der Säuren mit dem Erdalkalimetallhydroxid und/oder -oxid in einem Kohlenwasserstofflösungsmittel bereitet wird.
- 30 10. Verfahren nach Anspruch 9, worin das Kohlenwasserstofflösungsmittel unter Benzol, Toluol, Xylol oder einem Gemisch hiervon ausgewählt wird.
- 35 11. Verfahren nach einem der Ansprüche 1 bis 10, worin das Einführen von Kohlendioxid in Stufe (b) mit einer Geschwindigkeit von 0,05 bis 1,0 Äquivalent Kohlendioxid je Äquivalent Säure je Minute ausgeführt wird.
- 40 12. Verfahren nach einem der Ansprüche 1 bis 11, worin zwischen den Stufen (b) und (c) eine Alterungsperiode von 0,25 bis 20 Stunden vorgesehen wird.
13. Verfahren nach einem der Ansprüche 1 bis 12, worin die Stufen (a) und (b) in zwei Stufen ausgeführt werden, wobei die Stufen umfassen:
- 45 (a1) Bereiten eines Gemisches aus der Mischung von organischen Carbonsäuren mit mehr als einer äquivalenten Menge eines Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel;  
 (b1) Einführen von Kohlendioxid in das erhaltene Gemisch, bis wenigstens 0,5 Äquivalente Kohlendioxid je Äquivalent Erdalkalimetallüberschuß aufgenommen worden sind;  
 50 (a2) Zusetzen wenigstens eines weiteren Äquivalents an Erdalkalimetallhydroxid und/oder -oxid zum Reaktionsgemisch, sodaß die Gesamtmenge an Erdalkalimetallhydroxid und/oder -oxid wenigstens 10 Äquivalente beträgt;  
 (b2) Wiederaufnehmen der Einführung von Kohlendioxid in das gebildete Gemisch.
- 55 14. Basisches Erdalkalimetallsalz einer Mischung von organischen Carbonsäuren, hergestellt nach einem der Ansprüche 1 bis 13.

15. Ölzusammensetzung mit einem Hauptanteil an einem Grundöl und einem Nebenanteil an einem basischen Erdalkalimetallsalz nach Anspruch 14.

**Patentansprüche für folgenden Vertragsstaat : ES**

- 5 1. Verfahren zur Herstellung von basischen Erdalkalimetallsalzen von organischen Carbonsäuren, welches Verfahren
  - (a) ein Mischen der organischen Carbonsäuren, mit mehr als einer äquivalenten Menge eines Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel;
  - 10 (b) ein Einführen von Kohlendioxid in das erhaltene Gemisch in einer Menge von wenigstens 0,5 Äquivalenten Kohlendioxid je Äquivalent Erdalkalimetallüberschuß; und
  - (c) Abtrennen etwaiger restlicher Feststoffe und einer wäßrigen Phase, sofern vorhanden, umfaßt; dadurch gekennzeichnet, daß die organischen Carbonsäuren ein Gemisch einer  $C_8-30$  Alkylsalicylsäure mit einer oder mit mehreren Alkancarbonsäuren umfaßt, worin der Alkylteil verzweigt ist und 4 bis 40 Kohlenstoffatome aufweist.
2. Verfahren nach Anspruch 1, worin die Alkylsalicylsäure 12 bis 26 Kohlenstoffatome in der Alkylgruppe aufweist.
- 20 3. Verfahren nach Anspruch 1 oder 2, worin der Alkylrest der Alkancarbonsäure ein tertiärer Alkylrest mit 8 bis 28 Kohlenstoffatomen ist.
4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Äquivalentverhältnis der  $C_8-30$  Alkylsalicylsäure:Alkancarbonsäure von 10:1 bis 1:10 beträgt.
- 25 5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Erdalkalimetall Calcium oder Magnesium ist.
6. Verfahren nach einem der Ansprüche 1 bis 5, worin die in Stufe (a) zugesetzte Menge an Erdalkalimetallhydroxid und/oder -oxid von 10 bis 25 Äquivalente je Äquivalent Säure beträgt.
- 30 7. Verfahren nach einem der Ansprüche 1 bis 6, worin das Gemisch in Stufe (a) zusätzlich ein sauerstoffhaltiges organisches Lösungsmittel und gegebenenfalls Wasser umfaßt.
8. Verfahren nach Anspruch 7, worin das sauerstoffhaltige organische Lösungsmittel ein  $C_1-5$  Alkohol ist.
- 35 9. Verfahren nach einem der Ansprüche 1 bis 8, worin das Gemisch aus der Mischung der organischen Carbonsäuren mit Erdalkalimetallhydroxid und/oder -oxid durch Vermischen der Säuren mit dem Erdalkalimetallhydroxid und/oder -oxid in einem Kohlenwasserstofflösungsmittel bereitet wird.
- 40 10. Verfahren nach Anspruch 9, worin das Kohlenwasserstofflösungsmittel unter Benzol, Toluol, Xylol oder einem Gemisch hievon ausgewählt wird.
11. Verfahren nach einem der Ansprüche 1 bis 10, worin das Einführen von Kohlendioxid in Stufe (b) mit einer Geschwindigkeit von 0,05 bis 1,0 Äquivalent Kohlendioxid je Äquivalent Säure je Minute ausgeführt wird.
- 45 12. Verfahren nach einem der Ansprüche 1 bis 11, worin zwischen den Stufen (b) und (c) eine Alterungsperiode von 0,25 bis 20 Stunden vorgesehen wird.
- 50 13. Verfahren nach einem der Ansprüche 1 bis 12, worin die Stufen (a) und (b) in zwei Stufen ausgeführt werden, wobei die Stufen umfassen:
  - (a1) Bereiten eines Gemisches aus der Mischung von organischen Carbonsäuren mit mehr als einer äquivalenten Menge eines Erdalkalimetallhydroxids und/oder -oxids in einem Kohlenwasserstofflösungsmittel;
  - 55 (b1) Einführen von Kohlendioxid in das erhaltene Gemisch, bis wenigstens 0,5 Äquivalente Kohlendioxid je Äquivalent Erdalkalimetallüberschuß aufgenommen worden sind;
  - (a2) Zusetzen wenigstens eines weiteren Äquivalents an Erdalkalimetallhydroxid und/oder -oxid zum Reaktionsgemisch, sodaß die Gesamtmenge an Erdalkalimetallhydroxid und/oder -oxid wenigstens

10 Äquivalente beträgt;

(b2) Wiederaufnehmen der Einführung von Kohlendioxid in das gebildete Gemisch.

14. Verfahren zur Herstellung einer Ölzusammensetzung, welches ein Vermischen eines Hauptanteils eines Grundöls mit einem Nebenanteil eines basischen Erdalkalimetallsalzes einer Mischung von organischen Carbonsäuren umfaßt, das nach einem Verfahren gemäß einem der vorstehenden Ansprüche hergestellt worden ist.

# Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, FR, GB, GR, IT, LI, LU, NL, SE

1. Procédé pour la préparation de sels basiques de métaux alcalino-terreux d'acides organiques carboxyliques qui consistent à
  - (a) mélanger les acides organiques carboxyliques avec une quantité équivalente d'un hydroxyde et/ou d'un oxyde de métal alcalino-terreux dans un solvant à base d'hydrocarbure.
  - (b) introduire le dioxyde de carbone dans le mélange obtenu en une quantité d'au moins 0,5 équivalent de dioxyde de carbone par équivalent de métal alcalino-terreux en excès; et
  - (c) éliminer les solides résiduels, s'il y en a, et la couche aqueuse, si elle existe;
 caractérisé en ce que les acides organiques carboxyliques consistent en un mélange d'un acide alkyl-salicyclique en C<sub>8</sub> à C<sub>30</sub> avec un ou plus d'un acide alkane-carboxylique dans lequel la partie alkyle est ramifiée et présente de 4 à 40 atomes de carbone.
2. Procédé selon la revendication 1, dans lequel l'acide alkyl-salicyclique présente de 12 à 26 atomes de carbone dans le groupe alkyle.
3. Procédé selon la revendication 1 ou 2, dans lequel la partie alkyle de l'acide alkane-carboxylique est une partie alkyle tertiaire renfermant de 8 à 28 atomes de carbone.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le rapport de l'acide alkyl-salicyclique en C<sub>8</sub> à C<sub>30</sub> à l'acide alkane-carboxylique se situe dans la gamme de 10:1 à 1:10.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le métal alcalino-terreux est le calcium ou le magnésium.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la quantité d'hydroxyde et/ou d'oxyde de métal alcalino-terreux, ajoutée à l'étape (a) est de 10 à 25 équivalents par équivalent d'acide.
7. Procédé selon l'une des revendications 1 à 6, dans lequel le mélange à l'étape (a) comporte en outre un solvant organique renfermant de l'oxygène et, facultativement, de l'eau.
8. Procédé selon la revendication 7, dans lequel le solvant organique renfermant de l'oxygène est un alcool en C<sub>1</sub> à C<sub>6</sub>.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le mélange de la masse d'acides organiques carboxyliques et d'hydroxyde et/ou d'oxyde de métal alcalino-terreux est préparé en mélangeant les acides et l'hydroxyde et/ou l'oxyde de métal alcalino-terreux dans un solvant à base d'hydrocarbure.
10. Procédé selon la revendication 9, dans lequel le solvant à base d'hydrocarbure est choisi parmi le benzène, le toluène, le xylène ou un mélange de ceux-ci.
11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel l'introduction de dioxyde de carbone à l'étape (b) est réalisée selon un taux de 0,05 à 1,0 équivalent de dioxyde de carbone par équivalent d'acide et par minute.
12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel on prévoit une période de vieillissement de 0,25 à 20 heures entre les étapes (b) et (c).

13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel les étapes (a) et (b) sont mises en oeuvre en deux stades, ces stades consistant à:

- (a1) préparer un mélange de la masse d'acides organiques carboxyliques avec plus d'une quantité équivalente d'un hydroxyde et/ou d'un oxyde de métal alcalino-terreux dans un solvant à base d'hydrocarbure;
- (b1) introduire le dioxyde de carbone dans le mélange obtenu jusqu'à ce qu'au moins 0,5 équivalent de dioxyde de carbone par équivalent de métal alcalino-terreux en excès ait été capté.
- (a2) ajouter au moins encore un équivalent d'hydroxyde et/ou d'oxyde de métal alcalino-terreux au mélange réactionnel, de façon que la quantité totale d'hydroxyde et/ou d'oxyde de métal alcalino-terreux soit d'au moins 10 équivalents;
- (b2) reprendre l'introduction de dioxyde de carbone dans le mélange résultant.

14. Les sels basiques d'un métal alcalino-terreux d'un mélange d'acides organiques carboxyliques, lorsqu'il est préparé selon l'une quelconque des revendications 1 à 13.

15. Composition d'huile comportant une quantité prépondérante d'huile de base et une quantité plus faible d'un sel basique de métal alcalino-terreux tel que revendiqué dans la revendication 14.

#### Revendications pour l'Etat contractant suivant : ES

1. Procédé pour la préparation de sels basiques de métaux alcalino-terreux d'acides organiques carboxyliques qui consistent à
  - (a) mélanger les acides organiques carboxyliques avec une quantité équivalente d'un hydroxyde et/ou d'un oxyde de métal alcalino-terreux dans un solvant à base d'hydrocarbure.
  - (b) introduire le dioxyde de carbone dans le mélange obtenu en une quantité d'au moins 0,5 équivalent de dioxyde de carbone par équivalent de métal alcalino-terreux en excès; et
  - (c) éliminer les solides résiduels, s'il y en a, et la couche aqueuse, si elle existe; caractérisé en ce que les acides organiques carboxyliques consistent en un mélange d'un acide alkyl-salicyclique en C<sub>8</sub> à C<sub>30</sub> avec un ou plus d'un acide alkane-carboxylique dans lequel la partie alkyle est ramifiée et présente de 4 à 40 atomes de carbone.
2. Procédé selon la revendication 1, dans lequel l'acide alkyl-salicyclique présente de 12 à 26 atomes de carbone dans le groupe alkyle.
3. Procédé selon la revendication 1 ou 2, dans lequel la partie alkyle de l'acide alkane-carboxylique est une partie alkyle tertiaire renfermant de 8 à 28 atomes de carbone.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le rapport de l'acide alkyl-salicyclique en C<sub>8</sub> à C<sub>30</sub> à l'acide-alkane carboxylique se situe dans la gamme de 10:1 à 1:10.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le métal alcalino-terreux est le calcium ou le magnésium.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la quantité d'hydroxyde et/ou d'oxyde de métal alcalino-terreux, ajoutée à l'étape (a) est de 10 à 25 équivalents par équivalent d'acide.
7. Procédé selon l'une des revendications 1 à 6, dans lequel le mélange à l'étape (a) comporte en outre un solvant organique renfermant de l'oxygène et, facultativement, de l'eau.
8. Procédé selon la revendication 7, dans lequel le solvant organique renfermant de l'oxygène est un alcool en C<sub>1</sub> à C<sub>6</sub>.
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le mélange de la masse d'acides organiques carboxyliques et d'hydroxyde et/ou d'oxyde de métal alcalino-terreux est préparé en mélangeant les acides et l'hydroxyde et/ou l'oxyde de métal alcalino-terreux dans un solvant à base d'hydrocarbure.

10. Procédé selon la revendication 9, dans lequel le solvant à base d'hydrocarbure est choisi parmi le benzène, le toluène, le xylène ou un mélange de ceux-ci.
- 5 11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel l'introduction de dioxyde de carbone à l'étape (b) est réalisée selon un taux de 0,05 à 1,0 équivalent de dioxyde de carbone par équivalent d'acide et par minute.
12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel on prévoit une période de vieillissement de 0,25 à 20 heures entre les étapes (b) et (c).
- 10 13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel les étapes (a) et (b) sont mises en oeuvre en deux stades, ces stades consistant à:
- 15 (a1) préparer un mélange de la masse d'acides organiques carboxyliques avec plus d'une quantité équivalente d'un hydroxyde et/ou d'un oxyde de métal alcalino-terreux dans un solvant à base d'hydrocarbure;
- (b1) introduire le dioxyde de carbone dans le mélange obtenu jusqu'à ce qu'au moins 0,5 équivalent de dioxyde de carbone par équivalent de métal alcalino-terreux en excès ait été capté.
- (a2) ajouter au moins encore un équivalent d'hydroxyde et/ou d'oxyde de métal alcalino-terreux au mélange réactionnel, de façon que la quantité totale d'hydroxyde et/ou d'oxyde de métal alcalino-terreux soit d'au moins 10 équivalents;
- 20 (b2) reprendre l'introduction de dioxyde de carbone dans le mélange résultant.
14. Procédé pour la préparation d'une composition d'huile, qui consiste à mélanger une quantité prépondérante d'huile de base et une quantité plus faible d'un sel basique de métal alcalino-terreux d'une masse mélangée d'acides organiques carboxyliques, préparée selon un procédé tel que revendiqué dans l'une quelconque des revendications précédentes.
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